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Liquid-impregnated porous polypropylene surfaces for liquid repellency

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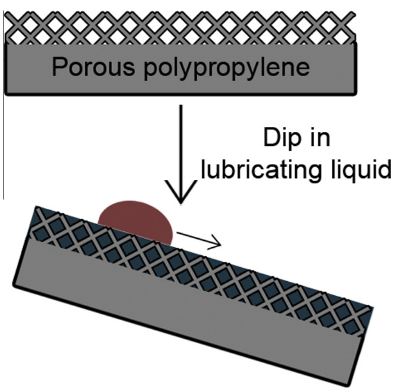
GRAPHICAL ABSTRACT



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ABSTRACT

Polypropylene is a popular plastic material used in consumer packaging. It would be desirable if such plastic containers were liquid repellent and not so easily fouled by their contents. Superomniphobic surfaces typically work by keeping the fouling liquid in a metastable state, with trapped pockets of air between the substrate and the liquid. An alternative method with greater long-term stability utilizes liquid-impregnated surfaces, where the liquid being repelled slides over an immiscible liquid immobilized on a porous surface. Here, we report a method for creating porous polypropylene surfaces amenable to liquid-impregnation. A solvent–nonsolvent polypropylene solution was deposited at high temperature to achieve the necessary porosity. Such surfaces were further functionalized with fluorosilane and dipped in the lubricating liquid to result in a durable, liquid-repellent surface. It is believed these liquid-impregnated surfaces will be more industrially viable than previous examples due to the ease of fabrication and their durability. These surfaces were found to exhibit repellency towards water, oils, shampoo, and laundry detergent with extremely low tilt angles due to the smooth liquid–liquid contact between the lubricating liquid and the liquid being repelled.

1. Introduction

Liquid repellency is a desirable surface property for a range of different applications including anti-fouling [1], self-cleaning, anti-smudge [2], and lab-on-chip [3] applications.

By selecting the correct chemistry and topography, a coating can display a variety of liquid wetting properties. This is typically

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achieved through enhancing the surface properties by addition of roughness. Hydrophobic surfaces, when roughened, become more hydrophobic [4]. Additionally, air can become trapped between the surface and the liquid creating a superhydrophobic surface [5]. To create superhydrophobic surfaces, inspiration can be taken from the lotus leaf, which combines hydrophobic waxes and hierarchical roughness to result in a water-repellent surface [6].

This is trivial for water but more difficult for lower surface tension liquids such as oils, since oil droplets are more likely to display contact angles of <90° on flat surfaces (oleophilic). High droplet contact angles via the Cassie-Baxter state of wetting can still be achieved, even if the contact angle on the flat surface (θ_{flat}) is low, through the use of re-entrant geometries, where surface asperities create an overhang (i.e. become narrower closer to the surface) [7–10].

However, one drawback of utilizing surface roughness and trapped air as seen in the Cassie-Baxter regime is that the liquid exists in a metastable state and liquid resting on such a surface can eventually penetrate into the roughness, transitioning from a Cassie-Baxter regime to a wetted state, referred to as the Wenzel regime. In doing so, the surface becomes wet by the liquid and is no longer repellent.

Another method of creating liquid-repellent surfaces is to take inspiration from the *Nepenthes* pitcher plants [11]. Pitcher plants are well known for their carnivorous nature and feature pitcher-shaped traps that have evolved to capture and digest insects. Many pitcher plants capture prey by utilizing a waxy zone along the pitcher rim (peristome). This wax attaches to the adhesive pads of the insect, which can no longer adhere to the plant wall and fall into the trap [12]. However, pitcher plants of the genus *Nepenthes* have been found to capture prey by a different mechanism, Fig. 1. In place of the waxy zone, the peristome of these pitcher plants features a regular microstructure that is wet by nectar and rainwater, resulting in a continuous liquid film over the surface of the rim. When wet, the peristome becomes extremely slippery and insects aquaplane across the surface and fall into the trap.

Artificial, liquid-impregnated surfaces inspired by the pitcher plant have previously been created. By adding to the surface a non-volatile liquid layer with a surface tension lower than that of the liquid being repelled, repellent surfaces can be created. The repellency of the surface is dependent upon the properties of the liquid layer and its miscibility with the liquids being repelled.

There are some requirements to ensure that the liquid-impregnated surfaces will be able to repel liquids. Firstly, they require surface topography features that ensure the lubricating liquid layer remains in place. This is achieved through the creation of a porous structure into which the impregnating liquid can wick. Second, the lubricating liquid must preferentially wet the solid surface. Untreated, the porous surface likely has a much higher surface energy than the fluorinated lubricating liquid (surface energy <20 mN m^{-1}). This means that, although the lubricating liquid coats the surface, there is little interaction between the two and a higher energy liquid that is added to the surface can displace the lubricating liquid. This can be mitigated by altering the chemistry of the porous structure through addition of a fluorosilane to match the chemistry of the lubricating liquid [13]. This ensures that the solid–liquid interaction of the lubricating liquid will not be replaced by a more favorable solid–liquid interaction of the liquid being repelled. Finally, the lubricating liquid and the liquid to be repelled must be immiscible. If the two liquids are immiscible, the result is atomically flat liquid–liquid contact, which causes the repelled droplet to slide across the lubricating film with very little tilting of the surface.

Previous examples of liquid-impregnated surfaces have several drawbacks that potentially limit their applicability to a range of scenarios. For instance, an early example utilized random Teflon nanofibres or epoxy-molded nanoposts as the porous solid surface [13]. These examples made for good model surfaces but their composition, fragility, and cost makes them unsuitable for certain real world applications.

Another issue with previous examples is the requirement for specific substrates. For instance, one example utilized colloidal templating to create highly ordered porous monolayers. However, this technique requires the nanostructured film be bonded to glass or other oxide substrates, limiting its applicability [14]. Other examples requiring specific substrates include nano-textured alumina [15] and electrodeposited polypyrrole nanostructures [16].

Finally, one method more suited to a range of applications and substrates involves spray coating wax to form the porous layer [17]. The wax layer is sufficiently porous to be impregnated by the liquid layer, which is sprayed separately. The focus on spray coating means that this technique could be used in manufacturing processes, however, the durability of the porous wax coating remains unclear. Porous structures are likely to be more fragile than their planar equivalents and the long-term durability of the porous layer is crucial to ensure the lubricating liquid remains immobilized on the surface and is able to repel the liquid of interest.

In this paper, mechanically durable liquid-repellent polypropylene has been achieved through the creation of a liquid-

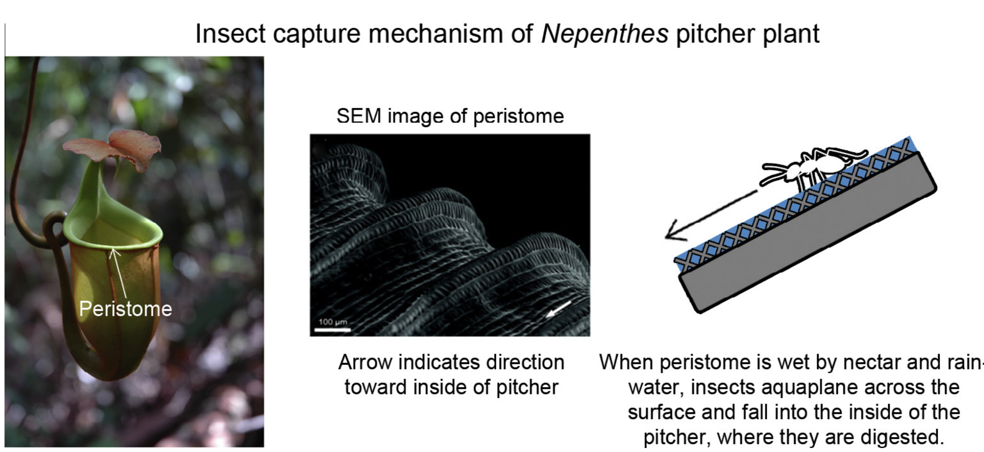

Fig. 1. Schematic to show mechanism for prey capture by *Nepenthes* pitcher plants. The rim of the pitcher (peristome) features surface features that become wet by nectar and rainwater. Insects landing on the wet peristome aquaplane across the surface and fall into the pitcher. Plant photograph by Natch Greyes. SEM image reproduced from Ref. [11] Copyright (2004) National Academy of Sciences.